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60 References to other related
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54 Electrode materials for rechargeable lithium batteries and process for their synthesis.

57 Lithium oxide compounds and transition metal compounds and their preparation are the object of the invention.

The compounds correspond to the formula $\text{Li}_{ny}(\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$, in which n is 1 or 2, and are characterized in that M and M' are identical or different and are selected from among transition metals, in that $0 < x \leq 1$, $0 < y \leq 1$, $1.8 \leq z \leq 2.2$, and in that said compound presents a specific surface area greater than $1.5 \text{ m}^2/\text{g}$.

A compound $\text{Li}_{ny}(\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$ is prepared by a process in which a mixture of precursors is prepared selected from the salts of metals M and M' , the mixture is dried and calcined, and is characterized in that the mixture of precursors is prepared in a liquid medium.

Application: electrode material for rechargeable lithium batteries.

The present invention has for object lithium oxide compounds and transition metal

compounds, their preparation and their application for the production of electrodes for batteries.

We are familiar with lithium cells and batteries. The so-called "lithium ion" batteries function according to the "rocking chair" principle according to which the lithium is transferred on the inside of the electro-chemical cell between two electrodes comprised of lithium insertion compounds, with a low electrical potential in the negative pole, and with a high electrical potential in the positive pole. They are comprised of active electrodes composed of a wide variety of materials. The positive electrode must be composed of a material which presents an elevated oxidation reduction potential and a high specific capacity or volumetric capacity, and which allows for good reversibility of the electrode reaction in the course of the charging cycles (oxidation) and the discharging cycles (reduction). Furthermore, it is desirable that said material not be toxic and that its cost be low.

Compounds of the LiMo_2 type, in which M represents Co, Ni and/or Mn, represent a good compromise between the above criteria. For example, we can cite the LiCoO_2 phases [R.J. Gummow et al., Mat. Res. Bull. 27 (1992), 327; H. Sekai et al., EP - 89 115 940.2; K. Mizushima et al., Mat. Res. Bull. 15 (1980), 783 and Solid State Ionics 3 - 4 (1981) 171; US- A- 4 302 518; US - A - 43 572 15; M..G. S. R. Thomas et al., J. Electrochem. Soc. 132 (1985) 132; J. J. Auborn et al., Proc. Symp. Lithium Batteries, (1986) p. 256]. We can also cite LiNiO_2 which has a weaker oxidizing ability as compared to a cobalt compound which would permit better stability for the electrolyte [J. R. Dahn et al., Solid State Ionics, 44 (1990) 87].

The classical preparation method for LiMO_2 compounds consists in a thermal treatment at between 700 and 900°C of a mixture of carbonates [Mizushima cited above; A. Mendiboure et al., Mat. Res. Bull. 19 (1984) 1382], of a mixture of cobalt and lithium oxides or hydroxides [A. Lecerf et al., EP - 89 110 158 and EPO 345 707] or of cobalt

acetates and lithium [J. R. Dahn et al., Solid State Ionics, 44 (1990) 87]. Even if the thermal treatment temperature is elevated, these methods based on the reactivity of powder mixtures in the solid phase require thermal treatments that are long in duration in order to ensure chemical homogenization and good crystallinity of the final LiMO_2 product. The "carbonate" method, for example, requires calcination with air at 900°C . A calcination method was then tried at a lower temperature, but the performance values of the yielded LiCoO_2 revealed themselves not to be as good as those values obtained for the compound at 900°C [J. R. Dahn et al., J. Electrochem. Soc. 138 (1991) 2207]. The method with "oxides" covers a calcination done at 700°C ; the performance values of the yielded products are analogous to those values for the classical compounds [A. Lecerf, cited above]. The method with "acetates" made it possible to lower the temperature of calcination to 300°C [P. Barboux et al., J. Solid State Ionics, 94 (1991) 158].

Nevertheless, the thermal treatment put into use in the anterior state of the art processes favors crystalline growth of the powders whose grain size generally ranges around a few microns and the specific surface area runs at about $1 \text{ m}^2/\text{g}$, measured by the BET [Brunauer Emmett Teller] method.

The object of the present invention is to provide a material capable of being used as a material for the production of positive and/or negative electrodes for a lithium battery or a lithium cell exhibiting improved performance values in terms of the anterior state of the art materials and capable of being obtained at a lesser cost.

To this end, the present invention has the object of providing compounds that are lithium oxides and transition metal oxides, providing a process to obtain such compounds as well as the application of these compounds to produce a positive electrode and a negative electrode in a battery or in a cell made of lithium.

A compound in accordance with the invention, which corresponds to the formula $\text{Li}_{ny}(\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$, in which n is equal to 1 or 2, is characterized in that M and M' are identical or different and are selected from among transition metals, in that $0 < x \leq 1$, $0 < y \leq 1$, $1.8 \leq z \leq 2.2$, and in that said compound presents a specific surface area greater than $1.5 \text{ m}^2/\text{g}$.

A compound in which M and/or M' is/are selected from among Ti, V, Mn, Cr, Fe, Co, Ni, Zr, Nb, Ta, W, while Mo and Re are particularly preferred.

Preferably, the specific surface area of the compounds of the present invention, determined by the BET method, is included within a range of 1.5 to 50 m²/g.

In the following text, the compounds of the invention for which $n = 1$ shall be designated by LiMO₂ and the compounds for which $n = 2$ shall be designated by spinels.

The preparation process for the $\text{Li}_{ny}\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$ compounds of the present invention is a process in which a mixture of precursors is prepared, selected from among the M and M' metal salts in question; it is dried and it is calcined. It is characterized in that the precursor mixture is prepared in a liquid medium.

Among the salts that can be used as precursors, we can cite carbonates, oxides, hydroxides, acetates, nitrates, oxalates, alcoholates and alkoxides.

The preparation of the precursor mixture in a liquid medium includes a step in which the precursors are placed into a solution and/or into a suspension in an appropriate solvent. After this, the mixture is extracted from the liquid medium, dried and calcined. Preferably, the solvent is selected from among water and alcohols in C₁ to C₄.

In a mode of implementation of the invention process, the precursor mixture is extracted from the liquid medium and is dried by spray drying. This process consists in spraying the solution or the suspension in an air or nitrogen atmosphere that is maintained at a temperature which is sufficient for the solvent to evaporate. In this manner, dried crystals are obtained which are then subjected to calcination which allows us to obtain a compound in accordance with the invention.

In another mode of implementation, the precursor mixture is extracted from the liquid medium by joint spray-drying/calcination. This process consists in spraying the solution or the suspension in an atmosphere of air or nitrogen brought up to the temperature of calcination. Drying and calcination are simultaneous. In this manner, a compound in accordance with the present invention is obtained directly.

Furthermore, in a third mode of implementation, the precursor mixture is extracted from the liquid medium by cryo-dessication. This process consists in bringing the medium to a temperature that is lower than the freezing temperature, then in placing the frozen medium under vacuum. The dried precursor mixture obtained by sublimation of

the solvent is then calcined.

When the precursors introduced into the liquid medium react together in such manner as to form a co-precipitate, the co-precipitate can be extracted from the liquid medium by filtration. The obtained precipitate can then be dried and calcined by a conventional process.

When the introduction of the precursors into the liquid medium does not lead to the formation of a precipitate, it is possible to introduce a precipitation agent into said liquid medium. The co-precipitate obtained in this manner is extracted by filtration, then washed in order to eliminate the cation originating from the precipitation agent. After this, the obtained washed precipitate can be dried and calcined by conventional processes. It can also be returned into the suspension in water and treated by the drying process and/or by the calcination process described above. That is to say, the suspension can be subjected to spray drying, followed by calcination, then by cryo-dessication followed by calcination or once more by spray drying/calcination.

Calcination of dried precursor mixtures according to conventional methods is conducted in an oxidizing atmosphere.

The use of precursor mixtures obtained in a liquid medium when implementing the process of the present invention allows for conducting calcination at a lower temperature and/or for a duration that is shorter than that of the processes in the anterior art. The parameters for calcination are selected in such a manner that a specific surface area is obtained which is included between 1.5 and 50 m²/g.

The compounds of the present invention are useful for the production of electrodes for lithium batteries. The use of the compounds of the present invention for the production of positive electrodes is particularly interesting. In fact, said compounds allow for increasing the specific surface area of the electrode, and as a result, the power density of the battery comprising said electrode which constitutes a desirable advantage for this application.

Furthermore, it is desirable to lower the potential of the positive electrode in order to avoid degradation of the electrolyte during charging. Thus, a positive LiCoO₂ electrode presents an elevated potential which requires the use of a very stable electrolyte. An electrode constituted by the Li_yCo_{1-x}M_xO₂ compound, with M being Ni or Mn for

example, prepared in accordance with the process of the current invention, presents a less oxidizing potential which allows for limiting the degradation of the electrolyte.

The present invention is explained in greater detail with the help of embodiment examples below, provided merely as exemplifications, but not in the restrictive sense.

The examples 1 through 6 concern the preparation of oxide compounds.

EXAMPLE 1

Li_yCoO_2 preparation

An aqueous solution containing 176.2 g/l of lithium hydroxide (LiOH , H_2O) was prepared under agitation at 100°C . To this solution, 0.8 l of an aqueous CoCl_2 solution was added at 125.5 g/l while maintaining a pH value at a value lower than 4 by the addition of hydrochloric acid, the final pH being 3.7. The obtained mixture was then heated to 100°C . Parallel to this, 426.8 g of sodium carbonate was dissolved in 1 liter of water and the two solutions were gradually mixed together. After agitating for 2 hours at 100°C , it was filtered then returned into suspension in 2 liters of water. The operation of returning it into suspension and filtering was repeated three times.

Various samples of the obtained precipitate were then calcined in a muffle furnace and air swept. The precipitate cake was treated in a static bed in a boat equipped either with or without a lid. The rise in temperature in order to attain the threshold was either slow (about 2 hours), or rapid (about 30 minutes).

All of the obtained compounds while observed under an electronic scanning microscope present a platelet surface and their x-ray diffraction diagram makes the characteristic LiCoO_2 stripes visible in conformity with the ASTM 16-0427 sheet.

Other characteristics of the products obtained under various conditions of calcination are provided in table 1 below.

TABLE 1

conditions of calcination					characteristics	
test number	temperature (°C)	duration of threshold (h)	rise in temperature	lid	BET surface (m ² /g)	size of grains (:m)
LC1	550	0.5	slow	no	-	-
LC2	550	1	slow	yes	-	≈ 0.3
LC3	550	2.3	slow	no	14.61	≈0.1
LC4	650	2	rapid	no	2.99	≈ 0.3

EXAMPLE 2

Preparation of $\text{Li}_y\text{Co}_{0.3}\text{Ni}_{0.7}\text{O}_2$ and $\text{Li}_y\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_2$ compounds

We reproduced the mode of operation implemented in example 1 while adding nickel chloride to the cobalt chloride solution at a quantity such that the desirable stoichiometry could be obtained.

Calcination of the obtained precipitate was conducted in the same manner as in example 1.

All of the obtained compounds while observed under an electronic scanning microscope present a platelet surface and their x-ray diffraction diagram makes the characteristic Li_yMo_2 stripes visible.

Other characteristics of the products obtained under various conditions of calcination are provided in table 2 below.

TABLE 2

conditions of calcination					characteristics	
test number	temperature (°C)	duration of threshold (h)	rise in temperature	lid	BET surface (m ² /g)	size of grains (:m)
LCN1	550	2	slow	yes	19.01	≈0.1

LCN2	650	2	rapid	yes	2.56	≈ 0.3
LCN3	550	2	slow	yes	17.53	≈ 0.2
LCN7	650	2	rapid	yes	1.66	≈ 0.5

EXAMPLE 3

Preparation of $\text{Li}_y\text{Mn}_2\text{O}_4$ compounds

We reproduced the mode of operation implemented in example 1 by replacing the cobalt chloride with manganese chloride.

Calcination of the obtained precipitate was conducted in the same manner as in example 1, at a temperature of 650°C .

The obtained compound while observed under an electronic scanning microscope presents a platelet surface and its x-ray diffraction diagram makes the characteristic $\text{Li}_y\text{Mn}_2\text{O}_4$ stripes visible.

The grain size of the compound obtained is about $0.3 \mu\text{m}$ and its BET specific surface area is $7.85 \text{ m}^2/\text{g}$.

EXAMPLE 4

Preparation of $\text{Li}_y\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ compounds

We reproduced the mode of operation implemented in example 3 while adding nickel chloride to the manganese chloride solution at a quantity such that the desirable stoichiometry could be obtained.

Calcination of the obtained precipitate was conducted in the same manner as in example 1.

All of the obtained compounds while observed under an electronic scanning microscope present a platelet surface and their x-ray diffraction diagram makes the characteristic

Li_yMo_2 and $\text{Li}_y\text{M}_2\text{O}_4$ stripes visible.

Other characteristics of the products obtained under various conditions of calcination are provided in table 3 below.

TABLE 3

conditions of calcination					characteristics	
test number	temperature (°C)	duration of threshold (h)	rise in temperature	lid	BET surface (m ² /g)	size of grains (:m)
LMN1	650	2	rapid	yes	36	≈0.1
LMN2	750	2.3	rapid	yes	20	≈0.3

The examination of the characteristics of the various compounds obtained after calcination demonstrates the minute grain sizes (less than 1 :m) and confirms the large specific surface area (greater than 1.5 m²/g) in relation to the characteristics of the compounds from the anterior art.

EXAMPLE 5

Preparation of LiCoO₂ compound by joint spray - drying

Lithium hydroxide (LiOH- H₂O) was dissolved in a solution of cobalt acetate in the presence of acetic acid in such a manner as to maintain a pH value of less than 4. The relative proportions of salts are such that the atomic ratio of Li/ Co is equal to 1.

Spray drying of this solution yields co-crystallized salts which present themselves in the form of spherical granules of about 30 :m in diameter. Samples of these salts were calcined under various conditions.

The obtained compounds while observed under an electronic scanning microscope presents a platelet surface and their x-ray diffraction diagram makes the characteristic Li_yMO₂ stripes visible.

Other characteristics of these compounds are provided in table 4 below.

TABLE 4

conditions of calcination					characteristics	
test number	temperature (°C)	duration of threshold (h)	rise in temperature	lid	BET surface (m ² /g)	size of grains (:m)
LC5	580	3.10	slow	yes	10.49	≈0.3

LC6	550	1.30	slow	no	2.48	-
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EXAMPLE 6

Preparation of LiCoO_2 compound by joint spray - drying

A moist cobalt hydroxide cake was placed in suspension in a solution of lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) and mixed. The relative proportions of the hydroxides were such that the atomic ratio of Li/ Co was equal to 1. The concentration of solid matter was adjusted in such a manner as to obtain the necessary fluidity for good spray drying.

Spray drying of this solution yielded spherical granules of 15 to 50 :m. The granules contain 5.47 % Li and 48 % Co. The samples of these granules were calcined under various conditions.

The obtained compounds have a lamellar structure confirmed by electronic scanning microscope, and their x-ray diffraction diagram makes the characteristic Li_yMO_2 stripes visible.

Other characteristics of these compounds are provided in table 5 below.

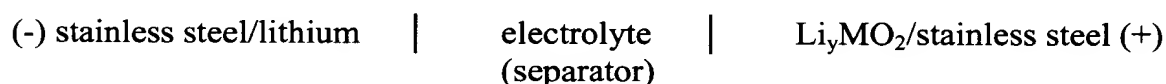
TABLE 5

conditions of calcination					characteristics	
test number	temperature (°C)	duration of threshold (h)	rise in temperature	lid	BET surface (m^2/g)	size of grains (:m)
LC7	560	2.15	slow	yes	35.52	≈ 0.1
LC8	550	2.00	slow	no	13.72	-

The examples 7 through 9 below refer to electrochemical tests.

Button type (CR 2430) electrochemical cells were produced with an external diameter of 24 mm and a thickness of 3 mm. The negative pole is comprised by a metallic lithium disk with a diameter of 20 mm cut from a sheet of 200 :m in thickness (commercially available from the Lithco Corporation). The separator is a disk cut from a sheet of microporous polypropylene supplied under the brand name of Celgard 2400 by

the Sanyo Corporation. The electrolyte is obtained by dissolving lithium salt, LiBF_4 , in a mixture comprised of propylene carbonate, ethylene carbonate and of dimethoxy ethane. The positive electrode is a composite electrode. It is comprised of a pellet of 8 mm in diameter obtained by compression under 2 tons/cm^2 of a mixture of Li_yMO_2 , of acetylene black, which improves electrode conductivity, and of poly (oxyethylene) which serves as a bonding agent. The total weight of the dried pellet is in the order of 30 to 50 mg which corresponds to a theoretical capacity of 4 to 7 mAh for the battery. Stainless steel disks are used as power leads in such a manner that the electrochemical chain corresponds to the following diagram:



The charging/ discharging tests were conducted under a static galvanic load, the voltage was limited to 4.2 V while charging and to 3.2 V while discharging. Current intensity was selected in a manner such that the total theoretical capacity be attained within 10 hours (load C/ 10). The calculation of this capacity is based on the hypothesis of an exchange of 0.5 Li per unit of MO_2 in the course of the cycles, which corresponds to a composition included between LiMO_2 and $\text{Li}_{0.5}\text{MO}_2$.

Polarization tests were also conducted in order to verify the behavior of the electrochemical cell when it is subjected to a constant intensity of electrical current for a few minutes. The polarization tests were carried out at various current intensity values corresponding to the following loads of discharge in C/n (C represents the battery capacity

and n represents the duration required to obtain a full discharge): C/ 1,000, C/ 500, C/ 100, C/ 50, C/ 10, 1C and 2C, which signifies a duration of discharge ranging from 1,000 hours to $\frac{1}{2}$ hour.

EXAMPLE 7

Embodiment of an electrochemical cell containing LC8

An electrochemical cell having the above described structure was prepared with the LC 8 compound from example 6. This cell was subjected to a static galvanic cycle under

the conditions indicated above.

Figure 1 presents the general appearance of the first six cycles; figure 2 is an enlarged presentation of the second cycle. We confirm that charging was done within 9.5 hours and discharging within 9 hours, both of which are durations that closely approximate the theoretical duration of 10 hours.

The Faraday output of the cycle is thus $9/9.5 \times 100$, or in the order of 95 %.

The minimum quantity of lithium exchanged in the course of the discharge represents 90 % of the theoretical value which corresponds to a variation Δx of the x content in Li_xCoO_2 of 0.45 (between 1 and 0.55 instead of between the theoretical 1 and 0.5).

The mean values of the charging voltages and of the discharging (e) voltages are respectively of about 3.95 V and 3.90 V.

The energy output of the cycle is thus $95 \times 3.9 / 3.95$, or 93.8 %.

The energy density attained calculated by the relational formula that $D_E = \Delta x \cdot F \cdot e / 3.6 M$ is 480 Wh/KG for LiCoO_2 . ($F = 96,500 \text{ C}$; $M = \text{molar mass of } \text{LiCoO}_2$).

Figure 3 represents the polarization curves for charging and discharging that were obtained with the LC8 compound, the testing being conducted on a previously charged battery. The power density P is calculated according to the formula:

$$P = \frac{e \times Q}{n}$$

in which e represents the discharge potential, Q represents the theoretical mass capacity of LiCoO_2 ($\approx 134 \text{ mAh/gram}$), and n represents the discharge load (C/n). The maximum power density is obtained based on the last point on the discharge curve for which $n = 1$ and $e = 3.8 \text{ V}$:

$$P = \frac{3.8 \times 134}{1} = 509 \text{ W/KG}$$

EXAMPLE 8

Embodiment of an electrochemical cell containing LC4

An electrochemical cell having the above described structure was prepared with the LC 4 compound. This cell was subjected to a static galvanic cycle under the conditions

indicated above.

Figure 4 represents the fourth charging/ discharging cycle. We confirm that charging and discharging were each done within 9 hours.

Performance values were realized analogous to those for the cell in example 7.

EXAMPLE 9

Embodiment of an electrochemical cell containing $\text{Li}_y\text{Co}_{0.3}\text{Ni}_{0.7}\text{O}_2$

An electrochemical cell having the above described structure was prepared with the $\text{Li}_y\text{Co}_{0.3}\text{Ni}_{0.7}\text{O}_2$ compound. This cell was subjected to a static galvanic cycle under the conditions indicated above.

Figure 5 represents the second charging/ discharging cycle. We confirm that charging and discharging were respectively done within 8 hours and 7.4 hours.

The Faraday output of the cycle is thus $7.4/8 \times 100$, or in the order of 92.5 %.

The minimum quantity of lithium exchanged in the course of the discharge represents 74% of the theoretical value.

The mean values of the charging voltages and of the discharging (e) voltages are respectively of about 3.81 V and 3.48 V.

The energy output of the cycle is thus $92.5 \times 3.48 / 3.81$, or 84.7 %.

The energy density attained calculated by the relational formula that $D_E =)x.F.e/ 3.6$ M is 357 Wh/KG.

We thus confirm that by substituting 70% of the cobalt with nickel, there is not a very significant effect on the Faraday output, nor on the energy output, nor on the energy density, even if there is a slight reduction in the operating battery voltage, which ensures for better durability of the battery.

COMPARATIVE EXAMPLE

Two cells were produced in the same manner as above while using as positive electrode material a mixed oxide obtained by calcination of mixed precursors in the form of powders in the dried state, the powders being respectively carbonates (product A) and oxides (product B). The loads for charging/ discharging were set at C/ 10.

Figure 6 and 7 respectively represent the first six cycles obtained respectively with product A and product B. The total duration of the cycles (charging and discharging) is less than 10 hours with very strong slopes at the end of each operation. The exchanged capacity represents approximately 50 % of that obtained by using positive electrodes comprised of oxide compounds in the present invention.

CLAIMS

1. Compound corresponding to the formula $\text{Li}_{ny}(\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$ in which n is 1 or 2, characterized in that M and M' are identical or different and are selected from among transition metals, in that $0 < x \leq 1$, $0 < y \leq 1$, $1.8 \leq z \leq 2.2$, and in that said compound presents a specific surface area greater than $1.5 \text{ m}^2/\text{g}$.

2. Compound in accordance with claim 1, characterized in that the specific surface area is included between 1.5 and $50 \text{ m}^2/\text{g}$.

3. Compound in accordance with claim 1, characterized in that M and M' are selected from among Ti, V, Mn, Cr, Fe, Co, Ni, Zr, Nb, Ta, W, Mo and Re.

4. Preparation process for a $\text{Li}_{ny}(\text{M}_{1-x}\text{M}'_x)_n\text{O}_{nz}$ compound in accordance with claim 1, in which a mixture of precursors is prepared selected from among the metal salts M and M', it is dried and it is calcined, characterized in that the precursor mixture is prepared in a liquid medium..

5. Process in accordance with claim 4, characterized in that the salts are selected from among carbonates, oxides, hydroxides, acetates, nitrates, oxalates, alcoholates and alkoxides.

6. Process in accordance with claim 4, characterized in that the precursors are placed into solution and/or into suspension in an appropriate solvent.

7. Process in accordance with claim 4, characterized in that the mixture of precursors is extracted from the liquid medium and it is dried by spray - drying, and in that the obtained dried crystals are subjected to calcination.

8. Process in accordance with claim 4, characterized in that the mixture of precursors is extracted from the liquid medium by joint spray - drying/calcination.

9. Process in accordance with claim 4, characterized in that the mixture of precursors is extracted from the liquid medium by cryo-dessication and in that the obtained dried product is subjected to calcination.

10. Process in accordance with claim 4, characterized in that the precursors introduced into the liquid medium react among themselves in such a manner as to form a

co-precipitate, the co-precipitate obtained is extracted from the liquid medium by filtration, then it is dried and it is calcined.

11. Process in accordance with claim 4, characterized in that a precipitation agent is added to the precursor mixture in the liquid medium, the co-precipitate is extracted from the liquid medium by filtration, it is washed, then it is dried and it is calcined.

12. Process in accordance with claim 4, characterized in that the calcination is conducted in an oxidizing atmosphere.

13. Process in accordance with claim 6, characterized in that the solvent is selected from among water and alcohols in C₁ through C₄.

14. Electrode comprising a compound in accordance with claim 1 as an active material.

15. Lithium battery comprising as a positive electrode an electrode in accordance with claim 14.

16. Lithium battery comprising as a negative electrode an electrode in accordance with claim 14.

[refer to 7 original graphs]

1/4

Figure 1

e/V

T/h

Figure 2

e/V

T/h

2/4

Figure 3

Discharge

Charge

e/V

Figure 4

e/V

T/h

3/4

Figure 5

e/V

T/h

Figure 6

e/V

T/h

4/4

Figure 7

e/V

T/h

FRENCH REPUBLIC

NATIONAL INSTITUTE
of INDUSTRIAL PROPERTYPRELIMINARY RESEARCH REPORT
established on the basis of the last claims filed
prior to commencing research

National registration no.

FA 487773

FR 9304807

DOCUMENTS CONSIDERED TO BE RELEVANT		claims concerned in the examined request	
category	document citation with indication, if need be, of relevant sections		
X	US - A - 4 567 031 (BRIAN RILEY) * claims 1 - 18*	1 - 15	
A	GB - A - 2 087 858 (KOICHI MIZUSHIMA) *CLAIMS 1 - 9* -----	1 - 3, 16	TECHNICAL RESEARCH DOMAINS (INT. CLASS. 5)
			C01G H01M
Research completion date: January 7, 1994			Examiner LIBBERECHT, E
CITED DOCUMENT CATEGORIES		T: theory or principle as basis of E: patent document having the advantage of being dated as anterior to the application date and which was only published at this application date or at D: cited in the request L: cited for other reasons *: member of the same family, corresponding document	
X: particularly relevant by itself Y: particularly relevant in combination with another A: relevant in view of at least one claim or of the general O: non-written revelation P: interpolated document			